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TECHNICAL OPERATIONS SUPPORT III (TOPS III)
Task Order 0018: Nanostructured Graphene-Like Polymers

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14. ABSTRACT
A theoretical model from a fully thermodynamic standpoint has been developed to describe the response of polymeric composites that are subject to diffusion and chemical reactions due to hostile environmental conditions. The thermodynamic framework is very general and has been used to describe the disparate and diverse response by a large class of materials: viscoelastic fluids, inelasticity, crystallization of polymers, twinning, shape memory alloys, single crystal super alloys, and viscoelastic solids.

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1.0   INTRODUCTION

The objective of the proposed research is to develop predictive models characterizing the response due to deformation, diffusion and reaction in service environments for PMR-15 resin composites. The principal investigator has developed a theoretical model from a fully thermodynamic standpoint to describe the response of polymeric composites that are subject to diffusion and chemical reactions due to hostile environmental conditions. The thermodynamic framework is very general and has been used to describe the disparate and diverse response by a large class of materials: viscoelastic fluids (Rajagopal and Srinivasa (2000), Krishnan and Rajagopal (2004)), inelasticity (Rajagopal and Srinivasa (1998)), crystallization of polymers (Rao and Rajagopal (2001), twinning (Rajagopal and Srinivasa (1997)), Kannan et al. (2002)), shape memory alloys (Rajagopal and Srinivasa (1999)), single crystal super alloys (Prasad et al. (2005), Prasad et al. (2006)), and viscoelastic solids (Kannan and Rajagopal (2004)). There are two central ideas on which the framework is built. The first is that when a body undergoes an entropy producing process, the underlying natural configuration" of the body (see Rajagopal (1995) for a discussion of natural configuration) usually changes and the second, the constitutive relation that describes the response of a body, from amongst a competing class of possible response functions is one that maximizes the rate at which entropy is produced. In this work, using both these above ideas, a model is developed to describe the response of a viscoelastic polymeric solid due to its deformation when a fluid is diffusing through the solid, taking into account temperature effects. Such a model can be used to describe, in addition to PMR-15 resin composite, a whole host of viscoelastic polymer composites due to hostile environmental conditions, namely high temperature and the diffusion of moisture through the body.

2.0 DEVELOPMENT OF A VISCOELASTIC SOLID MODEL WITH DEGRADATION DUE TO TEMPERATURE

In this section, we shall first develop a model for the viscoelastic behavior of PMR-15. This model also accounts for degradation due to high temperatures.

2.1 Preliminaries

Let κ_R be the reference configuration and κ_t denote the current configuration. Then, the motion χ_{κ_R} is the one‑one mapping that assigns to each point $\mathbf{X} \in \kappa_R$, a point $\mathbf{x} \in \kappa_t$, at a time t, i.e.,

$$\mathbf{x} = \chi_{\kappa_R}(\mathbf{X}, t). \tag{1}$$

Let $\kappa_{p(t)}$ denote the natural configuration (stress‑free) configuration corresponding to κ_t. This natural configuration is reached instantaneously from the current configuration, by the body, upon removal of a load. The deformation gradient $\mathbf{F}$ is defined by

$$\mathbf{F} := \frac{\partial \chi_{\kappa_R}}{\partial \mathbf{X}}. \tag{2}$$

Let $\mathbf{F}_{\kappa_{p(t)}}$ be the gradient of the mapping from $\kappa_{p(t)}$ and let $\mathbf{G}$ be the gradient of mapping from κ_R to $\kappa_{p(t)}$ (see Figure 1). Then,

$$\mathbf{F} = \mathbf{F}_{\kappa_{p(t)}} \mathbf{G}, \tag{3}$$

or

$$\mathbf{G} = \mathbf{F}_{\kappa_{p(t)}}^{-1} \mathbf{F}. \tag{4}$$

We shall denote the left Cauchy‑Green stretch tensors

$$\mathbf{B}_G := \mathbf{G}\mathbf{G}^T, \quad \mathbf{B}_{p(t)} := \mathbf{F}_{\kappa_{p(t)}} \mathbf{F}_{\kappa_{p(t)}}^T. \tag{5}$$

We shall also define the velocity gradients

$$\mathbf{L}_G := \dot{\mathbf{G}}\mathbf{G}^{-1}, \quad \mathbf{L} = \dot{\mathbf{F}}\mathbf{F}^{-1}, \quad \mathbf{L}_p = \dot{\mathbf{F}}_{\kappa_{p(t)}} \mathbf{F}_{\kappa_{p(t)}}^{-1}, \tag{6}$$

with their symmetric parts by

$$\mathbf{D}_i = \frac{1}{2}\left(\mathbf{L}_i + \mathbf{L}_i^T\right), \quad i = p(t), G \text{ or no subscript.} \tag{7}$$

Also, we define

$$I_{\mathbf{B}_l} = tr(\mathbf{B}_l), \quad II_{\mathbf{B}_l} = \frac{1}{2}\left[(tr(\mathbf{B}_l))^2 - tr(\mathbf{B}_l^2)\right], \quad l = G, p(t), \tag{8}$$

where $tr(.)$ is the trace operator for a second order tensor. Now,

$$\begin{aligned}
\dot{\mathbf{F}} &= \dot{\mathbf{F}}_{\kappa_{p(t)}} \mathbf{G} + \mathbf{F}_{\kappa_{p(t)}} \dot{\mathbf{G}} \\
\Rightarrow \dot{\mathbf{F}}\mathbf{F}^{-1} &= \dot{\mathbf{F}}_{\kappa_{p(t)}} \mathbf{G}\mathbf{G}^{-1}\mathbf{F}_{\kappa_{p(t)}}^{-1} + \mathbf{F}_{\kappa_{p(t)}} \dot{\mathbf{G}} \\
\Rightarrow \mathbf{L} &= \mathbf{L}_{p(t)} + \mathbf{F}_{\kappa_{p(t)}} \mathbf{L}_G \mathbf{F}_{\kappa_{p(t)}}^{-1},
\end{aligned} \tag{9}$$

where $\dot{(.)}$ is the time derivative of the second order tensor. In addition,

where $\dot{(\cdot)}$ is the time derivative of the second order tensor. In addition,

$$\dot{\mathbf{B}}_{p(t)} = \dot{\mathbf{F}}_{\kappa_{p(t)}}\mathbf{F}^T + \mathbf{F}\dot{\mathbf{F}}_{\kappa_{p(t)}}^T$$
$$= \mathbf{L}_{p(t)}\mathbf{B}_{p(t)} + \mathbf{B}_{p(t)}\mathbf{L}_{p(t)}^T, \tag{10}$$

and similarly

$$\dot{\mathbf{B}}_G = \mathbf{L}_G\mathbf{B}_G + \mathbf{B}_G\mathbf{L}_G^T. \tag{11}$$

Hence, from (9) and (10), we have

$$\dot{\mathbf{B}}_{p(t)} = \mathbf{L}\mathbf{B}_{p(t)} + \mathbf{B}_{p(t)}\mathbf{L}_{p(t)}^T - \mathbf{F}_{\kappa_{p(t)}}\left(\mathbf{L}_G + \mathbf{L}_G^T\right)\mathbf{F}_{\kappa_{p(t)}}^T, \tag{12}$$

and so

$$\overset{\nabla}{\mathbf{B}}_{p(t)} = -2\mathbf{F}_{\kappa_{p(t)}}\mathbf{D}_G\mathbf{F}_{\kappa_{p(t)}}^T, \tag{13}$$

where $\overset{\nabla}{(\ )}$ is the Oldroyd derivative. The non‑isothermal *reduced energy dissipation equation* (Kannan and Rajagopal (2004)) is given by:

$$\mathbf{T}.\mathbf{D} - \rho\dot{\psi} - \rho s\dot{\theta} - \frac{\mathbf{q}_h.\text{grad}\,\theta}{\theta} = \rho\theta\zeta := \xi \geq 0, \tag{14}$$

where $\mathbf{T}$ is the Cauchy stress, ψ is the specific Helmoltz free energy, ρ is the density of viscoelastic solid, θ is the temperature, s is the specific entropy, $\mathbf{q}_h$ is the heat flux, ζ is the rate of entropy production and ξ is the rate of dissipation.

2.2 Constitutive assumptions and maximization of the rate of dissipation

2.2.1 General results

Now, we shall assume that the viscoelastic solid is isotropic and incompressible with the specific Helmoltz potential of the form

$$\psi = \psi(\mathbf{B}_{p(t)}, \mathbf{B}_G, \theta) = \hat{\psi}(I_{\mathbf{B}_{p(t)}}, II_{\mathbf{B}_{p(t)}}, I_{\mathbf{B}_G}, II_{\mathbf{B}_G}, \theta). \tag{15}$$

Based on the assumption of isotropic elastic response, we choose $\kappa_{p(t)}$ such that

$$\mathbf{F}_{\kappa_{p(t)}} = \mathbf{V}_{\kappa_{p(t)}}, \tag{16}$$

where $\mathbf{V}_{\kappa_{p(t)}}$ is the right stretch tensor in the polar decomposition of $\mathbf{F}_{\kappa_{p(t)}}$.

We shall also assume that the total dissipation can be split additively as follows

$$\mathbf{T}.\mathbf{D} - \rho\dot{\psi} - \rho s\dot{\theta} = \xi_m \geq 0, \quad -\frac{\mathbf{q}_h.\text{grad}\,\theta}{\theta} = \xi_c \geq 0, \tag{17}$$

where ξ_m, ξ_c are the rates of mechanical dissipation and dissipation due to conduction respectively. Now, we constitutively choose

$$\mathbf{q}_h = -k(\theta)\text{grad}\theta, \quad k(\theta) \geq 0, \tag{18}$$

where k is the thermal conductivity; so that (17(b)) is automatically satisfied.

Now,

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$$\dot{\psi} = \left[\left(\frac{\partial \hat{\psi}}{\partial I_{B_{p(t)}}} + I_{B_{p(t)}} \frac{\partial \hat{\psi}}{\partial II_{B_{p(t)}}} \right) \mathbf{I} - \frac{\partial \hat{\psi}}{\partial II_{B_{p(t)}}} \mathbf{B}_{p(t)} \right] . \dot{\mathbf{B}}_{p(t)}$$
$$+ \left[\left(\frac{\partial \hat{\psi}}{\partial I_{B_G}} + I_{B_G} \frac{\partial \hat{\psi}}{\partial II_{B_G}} \right) \mathbf{I} - \frac{\partial \hat{\psi}}{\partial II_{B_G}} \mathbf{B}_G \right] . \dot{\mathbf{B}}_G + \frac{\partial \hat{\psi}}{\partial \theta} \dot{\theta}, \tag{19}$$

and using (10), (11) along with (16) in (19)

$$\dot{\psi} = 2 \left[\left(\frac{\partial \hat{\psi}}{\partial I_{B_{p(t)}}} + I_{B_{p(t)}} \frac{\partial \hat{\psi}}{\partial II_{B_{p(t)}}} \right) \mathbf{B}_{p(t)} - \frac{\partial \hat{\psi}}{\partial II_{B_{p(t)}}} \mathbf{B}_{p(t)}^2 \right] . (\mathbf{D} - \mathbf{D}_G)$$
$$+ 2 \left[\left(\frac{\partial \hat{\psi}}{\partial I_{B_G}} + I_{B_G} \frac{\partial \hat{\psi}}{\partial II_{B_G}} \right) \mathbf{B}_G - \frac{\partial \hat{\psi}}{\partial II_{B_G}} \mathbf{B}_G^2 \right] . \mathbf{D}_G + \frac{\partial \hat{\psi}}{\partial \theta} \dot{\theta}. \tag{20}$$

Also, we assume the mechanical rate of dissipation to be of the form

$$\xi_m = \xi_m(\theta, \mathbf{B}_{p(t)}, \mathbf{D}_G). \tag{21}$$

On substituting (20) into (17(a))

$$\left[\mathbf{T} - 2\rho \left(\frac{\partial \hat{\psi}}{\partial I_{B_{p(t)}}} + I_{B_{p(t)}} \frac{\partial \hat{\psi}}{\partial II_{B_{p(t)}}} \right) \mathbf{B}_{p(t)} + 2\rho \frac{\partial \hat{\psi}}{\partial II_{B_{p(t)}}} \mathbf{B}_{p(t)}^2 \right] . \mathbf{D}$$
$$+ 2\rho \left[\left(\frac{\partial \hat{\psi}}{\partial I_{B_{p(t)}}} + I_{B_{p(t)}} \frac{\partial \hat{\psi}}{\partial II_{B_{p(t)}}} \right) \mathbf{B}_{p(t)} - \frac{\partial \hat{\psi}}{\partial II_{B_{p(t)}}} \mathbf{B}_{p(t)}^2 \right] . \mathbf{D}_G$$
$$- 2\rho \left[\left(\frac{\partial \hat{\psi}}{\partial I_{B_G}} + I_{B_G} \frac{\partial \hat{\psi}}{\partial II_{B_G}} \right) \mathbf{B}_G - \frac{\partial \hat{\psi}}{\partial II_{B_G}} \mathbf{B}_G^2 \right] . \mathbf{D}_G$$
$$- \rho \left[\frac{\partial \hat{\psi}}{\partial \theta} + s \right] \dot{\theta}$$
$$= \xi_m(\theta, \mathbf{B}_{p(t)}, \mathbf{D}_G). \tag{22}$$

We shall choose

$$s = -\frac{\partial \hat{\psi}}{\partial \theta}, \tag{23}$$

and define

$$\mathbf{T}_{p(t)} := p_1 \mathbf{I} + 2\rho \left[\left(\frac{\partial \hat{\psi}}{\partial I_{B_{p(t)}}} + I_{B_{p(t)}} \frac{\partial \hat{\psi}}{\partial II_{B_{p(t)}}} \right) \mathbf{B}_{p(t)} - \frac{\partial \hat{\psi}}{\partial II_{B_{p(t)}}} \mathbf{B}_{p(t)}^2 \right], \tag{24}$$

$$\mathbf{T}_G := p_2 \mathbf{I} + 2\rho \left[\left(\frac{\partial \hat{\psi}}{\partial I_{B_G}} + I_{B_G} \frac{\partial \hat{\psi}}{\partial II_{B_G}} \right) \mathbf{B}_G - \frac{\partial \hat{\psi}}{\partial II_{B_G}} \mathbf{B}_G^2 \right], \tag{25}$$

where p_1, p_2 are the Lagrange multipliers. Using (23)–(25) in (22)

$$\left(\mathbf{T} - \mathbf{T}_{p(t)} \right) . \mathbf{D} + \left(\mathbf{T}_{p(t)} - \mathbf{T}_G \right) . \mathbf{D}_G$$
$$= \xi_m(\theta, \mathbf{B}_{p(t)}, \mathbf{D}_G). \tag{26}$$

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From constraint of incompressibility, we have

$$tr(\mathbf{D}) = tr(\mathbf{D}_{p(t)}) = tr(\mathbf{D}_G) = 0. \tag{27}$$

Since, RHS of Eqn.(26) does not depend on $\mathbf{D}$, using (27),

$$\mathbf{T} = p\mathbf{I} + \mathbf{T}_{p(t)}, \tag{28}$$

where p is the Lagrange multiplier due to incompressibility, with

$$\left(\mathbf{T}_{p(t)} - \mathbf{T}_G\right).\mathbf{D}_G = \xi_m(\mathbf{B}_{p(t)}, \mathbf{D}_G), \tag{29}$$

which can be re‑written as

$$(\mathbf{T} - \mathbf{T}_G).\mathbf{D}_G = \xi_m(\mathbf{B}_{p(t)}, \mathbf{D}_G), \tag{30}$$

using (27) and (28) .

Now, following Rajagopal and Srinivasa (2000), we maximize the rate of dissipation ξ_m by varying $\mathbf{D}_G$ for fixed $\mathbf{B}_{p(t)}$. For this, we maximize the function

$$\Phi := \xi_m + \lambda_1 \left[\xi_m - (\mathbf{T} - \mathbf{T}_G).\mathbf{D}_G\right] + \lambda_2(\mathbf{I}.\mathbf{D}_G), \tag{31}$$

where λ_1, λ_2 are the Lagrange multipliers. By setting, $\partial\Phi/\partial\mathbf{D}_G = 0$, we get

$$\mathbf{T} = \mathbf{T}_G + \frac{\lambda_2}{\lambda_1}\mathbf{I} + \left(\frac{\lambda_1 + 1}{\lambda_1}\right)\frac{\partial\xi_m}{\partial\mathbf{D}_G}. \tag{32}$$

On substituting (32) in (30) we get

$$\left(\frac{\lambda_1 + 1}{\lambda_1}\right) = \frac{\xi_m}{\frac{\partial\xi_m}{\partial\mathbf{D}_G}.\mathbf{D}_G}, \tag{33}$$

and so (32) with (25) becomes

$$\mathbf{T} = 2\rho\left[\left(\frac{\partial\hat{\psi}}{\partial I_{B_G}} + I_{B_G}\frac{\partial\hat{\psi}}{\partial II_{B_G}}\right)\mathbf{B}_G - \frac{\partial\hat{\psi}}{\partial II_{B_G}}\mathbf{B}_G^2\right] + \left(\frac{\xi_m}{\frac{\partial\xi_m}{\partial\mathbf{D}_G}.\mathbf{D}_G}\right)\frac{\partial\xi_m}{\partial\mathbf{D}_G} + \hat{\lambda}\mathbf{I}. \tag{34}$$

where $\hat{\lambda} := \frac{\lambda_2}{\lambda_1} + p_2$ is the Lagrange multiplier due to the constraint of incompressibility.

Finally, the constitutive relations for the viscoelastic solid are given by

$$\mathbf{T} = p'\mathbf{I} + 2\rho\left[\left(\frac{\partial\hat{\psi}}{\partial I_{B_{p(t)}}} + I_{B_{p(t)}}\frac{\partial\hat{\psi}}{\partial II_{B_{p(t)}}}\right)\mathbf{B}_{p(t)} - \frac{\partial\hat{\psi}}{\partial II_{B_{p(t)}}}\mathbf{B}_{p(t)}^2\right],$$

$$\mathbf{T} = \hat{\lambda}\mathbf{I} + 2\rho\left[\left(\frac{\partial\hat{\psi}}{\partial I_{B_G}} + I_{B_G}\frac{\partial\hat{\psi}}{\partial II_{B_G}}\right)\mathbf{B}_G - \frac{\partial\hat{\psi}}{\partial II_{B_G}}\mathbf{B}_G^2\right] + \left(\frac{\xi_m}{\frac{\partial\xi_m}{\partial\mathbf{D}_G}.\mathbf{D}_G}\right)\frac{\partial\xi_m}{\partial\mathbf{D}_G}, \tag{35}$$

$$\mathbf{q}_h = -k(\theta)\mathrm{grad}\theta, \quad s = -\frac{\partial\hat{\psi}}{\partial\theta}.$$

2.2.2 Specific case

Specifically, we choose the stored energy as

$$\hat{\psi} = A^s + (B^s + c_2^s)(\theta - \theta_s) - \frac{c_1^s}{2}(\theta - \theta_s)^2 - c_2^s\theta\ln\left(\frac{\theta}{\theta_s}\right) + \frac{\mu_{G0} - \mu_{G1}\theta}{2\rho\theta_s}(I_{B_G} - 3) + \frac{\mu_{p0} - \mu_{p1}\theta}{2\rho\theta_s}(I_{B_{p(t)}} - 3), \tag{36}$$

where $\mu_{G0}, \mu_{G1}, \mu_{p0}, \mu p1$ are elastic constants, θ_s is a reference temperature for the viscoelastic solid and the rate of dissipation as

$$\xi_m = \eta(\theta) \left(\mathbf{D}_G . \mathbf{B}_{p(t)} \mathbf{D}_G\right)^m, \tag{37}$$

where η is the viscosity.

Now,

$$s = \frac{\partial \hat{\psi}}{\partial \theta} \tag{38}$$

$$= -(B^s + c_2^s) + c_1^s (\theta - \theta_s) + c_2^s \ln\left(\frac{\theta}{\theta_s}\right) + c_2^s + \frac{\mu_{G1}}{2\rho\theta_s}(I_{B_G} - 3) + \frac{\mu_{p1}}{2\rho\theta_s}(I_{B_{p(t)}} - 3). \tag{39}$$

$$\tag{40}$$

$$\epsilon = \psi + \theta s$$

$$= A^s - B^s \theta_s + c_2^s (\theta - \theta_s) + \frac{c_1^s}{2}\left(\theta^2 - \theta_s^2\right) + \frac{\mu_{G0}}{2\rho\theta_s}(I_{B_G} - 3) + \frac{\mu_{p0}}{2\rho\theta_s}(I_{B_{p(t)}} - 3). \tag{41}$$

and the specific heat capacity C_v is

$$C_v = -\epsilon\theta = c_1^s \theta + c_2^s. \tag{42}$$

Then, (35) reduces to

$$\mathbf{T} = p\mathbf{I} + \bar{\mu}_p \mathbf{B}_{p(t)},$$

$$\mathbf{T} = \lambda\mathbf{I} + \bar{\mu}_G \mathbf{B}_G + \frac{\eta}{2}\left(\mathbf{D}_G . \mathbf{B}_{p(t)} \mathbf{D}_G\right)^{m-1}\left(\mathbf{B}_{p(t)} \mathbf{D}_G + \mathbf{D}_G \mathbf{B}_{p(t)}\right), \tag{43}$$

where $\bar{\mu}_p = \frac{\mu_{p0} - \mu_{p1}\theta}{\theta_s}$, $\bar{\mu}_G = \frac{\mu_{G1} - \mu_{G0}\theta}{\theta_s}$. From (43)

$$(p - \lambda)\mathbf{I} + \bar{\mu}_p \mathbf{B}_{p(t)} = \bar{\mu}_G \mathbf{B}_G + \frac{\eta}{2}\left(\mathbf{D}_G . \mathbf{B}_{p(t)} \mathbf{D}_G\right)^{m-1}\left(\mathbf{B}_{p(t)} \mathbf{D}_G + \mathbf{D}_G \mathbf{B}_{p(t)}\right), \tag{44}$$

and so by pre‑multiplying the above equation by $\mathbf{B}_{p(t)}^{-1}$ and taking the trace, we get

$$(p - \lambda) = \frac{\bar{\mu}_G tr(\mathbf{B}_{p(t)}^{-1}\mathbf{B}_G) - 3\bar{\mu}_p}{tr(\mathbf{B}_{p(t)}^{-1})}. \tag{45}$$

Using (45) in (44), we arrive at the following evolution equation for the natural configuration

$$\left[\frac{\bar{\mu}_G tr(\mathbf{B}_{p(t)}^{-1}\mathbf{B}_G) - 3\bar{\mu}_p}{tr(\mathbf{B}_{p(t)}^{-1})}\right]\mathbf{I} + \bar{\mu}_p \mathbf{B}_{p(t)} = \bar{\mu}_G \mathbf{B}_G + \frac{\eta}{2}\left(\mathbf{D}_G . \mathbf{B}_{p(t)} \mathbf{D}_G\right)^{m-1}\left(\mathbf{B}_{p(t)} \mathbf{D}_G + \mathbf{D}_G \mathbf{B}_{p(t)}\right) \tag{46}$$

This is the evolution equation of the natural configuration. Thus, with the current choice of energy storage and rate of dissipation, we arrive at the following constitutive equations:

$$\mathbf{T} = p\mathbf{I} + \bar{\mu}_p \mathbf{B}_{p(t)} \tag{47}$$

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and

$$\left[\frac{\bar{\mu}_G tr(\mathbf{B}_{p(t)}^{-1}\mathbf{B}_G) - 3\bar{\mu}_p}{tr(\mathbf{B}_{p(t)}^{-1})}\right]\mathbf{I} + \bar{\mu}_p\mathbf{B}_{p(t)} = \bar{\mu}_G\mathbf{B}_G + \frac{\eta}{2}\left(\mathbf{D}_G.\mathbf{B}_{p(t)}\mathbf{D}_G\right)^{m-1}\left(\mathbf{B}_{p(t)}\mathbf{D}_G + \mathbf{D}_G\mathbf{B}_{p(t)}\right),$$

(48)

along with

$$\mathbf{D}_G = -\frac{1}{2}\mathbf{V}_{\kappa_{p(t)}}^{-1}\ \overset{\triangledown}{\mathbf{B}}_{p(t)}\ \mathbf{V}_{\kappa_{p(t)}}^{-1}$$

(49)

The above model reduces to the Maxwell fluid- like model derived by Rajagopal and Srinivasa (2000) when $m = 1$ and $\bar{\mu}_G = 0$.

2.2.3 Application of Model

We shall apply this model to a deformation that is homogeneous and in uniaxial compression/extension, given by

$$x = \lambda(t), \quad y = \frac{1}{\sqrt{\lambda(t)}}, \quad z = \frac{1}{\sqrt{\lambda(t)}}.$$

(50)

The velocity gradient is given by

$$\mathbf{L} = \operatorname{diag}\left\{\frac{\dot{\lambda}}{\lambda}, -\frac{\dot{\lambda}}{2\lambda}, -\frac{\dot{\lambda}}{2\lambda}\right\}.$$

(51)

We shall assume

$$\mathbf{B}_{p(t)} = \left\{B, \frac{1}{\sqrt{B}}, \frac{1}{\sqrt{B}}\right\}.$$

(52)

So,

$$\dot{\mathbf{B}}_{p(t)} = \operatorname{diag}\left\{\dot{B}, -\frac{\dot{B}}{2B^{3/2}}, -\frac{\dot{B}}{2B^{3/2}}\right\},$$

(53)

$$\overset{\triangledown}{\mathbf{B}}_{p(t)} = \operatorname{diag}\left\{\dot{B} - \frac{2B\dot{\lambda}}{\lambda}, -\frac{\dot{B}}{2B^{3/2}} + \frac{\dot{\lambda}}{\lambda\sqrt{B}}, -\frac{\dot{B}}{2B^{3/2}} + \frac{\dot{\lambda}}{\lambda\sqrt{B}}\right\},$$

(54)

$$\mathbf{V}_{\kappa_{p(t)}} = \operatorname{diag}\left\{\sqrt{B}, \frac{1}{B^{1/4}}, \frac{1}{B^{1/4}}\right\}$$

(55)

and

$$\mathbf{D}_G = -\frac{1}{2}\operatorname{diag}\left\{\frac{\dot{B}}{B} - \frac{2\dot{\lambda}}{\lambda}, \frac{\dot{\lambda}}{\lambda} - \frac{\dot{B}}{2B}, \frac{\dot{\lambda}}{\lambda} - \frac{\dot{B}}{2B}\right\}$$

(56)

Also,

$$\mathbf{G} = \mathbf{V}_{\kappa_{p(t)}}^{-1}\mathbf{F}$$
$$= \operatorname{diag}\left\{\frac{\lambda}{\sqrt{B}}, \frac{B^{1/4}}{\sqrt{\lambda}}, \frac{B^{1/4}}{\sqrt{\lambda}}\right\},$$

(57)

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which gives

$$\mathbf{B}_G = \text{diag}\left\{\frac{\lambda^2}{B}, \frac{\sqrt{B}}{\lambda}, \frac{\sqrt{B}}{\lambda}\right\}.$$

(58)

and

$$\mathbf{B}_{p(t)}^{-1}\mathbf{B}_G = \text{diag}\left\{\frac{\lambda^2}{B^2}, \frac{B}{\lambda}, \frac{B}{\lambda}\right\}.$$

(59)

Substituting (52), (54), (59) in (46) and for $m = 1$

$$\frac{\dot{B}}{2} = \frac{B\dot{\lambda}}{\lambda} + \frac{\bar{\mu}_G}{\eta}\frac{\lambda^2}{B} - \frac{\bar{\mu}_p}{\eta}B - \left\{\frac{\frac{\bar{\mu}_G}{\eta}\left(\lambda^3 + 2B^3\right) - 3\frac{\bar{\mu}_p}{\eta}\lambda B^2}{\lambda B\left(1 + 2B^{3/2}\right)}\right\}.$$

(60)

In general, we get the following evolution equation for the natural configuration

$$\dot{\lambda} = \lambda\left\{\frac{\dot{B}}{2B} - \left[\frac{1}{\eta B\left(B + \frac{1}{2\sqrt{B}}\right)^{m-1}}\left\{\bar{\mu}_G\frac{\lambda^2}{B} - \bar{\mu}_p B - \left(\frac{\bar{\mu}_G\left(\lambda^3 + 2B^3\right) - 3\bar{\mu}_p B^2\lambda}{B\lambda(1 + 2B^{3/2})}\right)\right\}\right]^{\frac{1}{2m-1}}\right\}$$

(61)

Now, plugging (52) into (47) and using the fact that lateral surfaces are traction free

$$T_{11} = \bar{\mu}_p\left(B - \frac{1}{\sqrt{B}}\right).$$

(62)

2.2.4 Comparison with experimental creep data

For the loading process, with known constant applied stress T_{11} and material properties, (62) was first solved for B(t). Then, (60) was solved with initial condition $\lambda(0) = B(0)$. For the unloading process, T_{11} was set to zero and B was evaluated using (62). Then using the initial condition $\lambda(t_i^+) = \lambda(t_i^-) - l$, where t_i is the time when unloading is started, l is the instantaneous elastic stretch, $\lambda(t)$ during the unloading process is evaluated using (60). All the calculations were done in Matlab using the "ode45" solver.
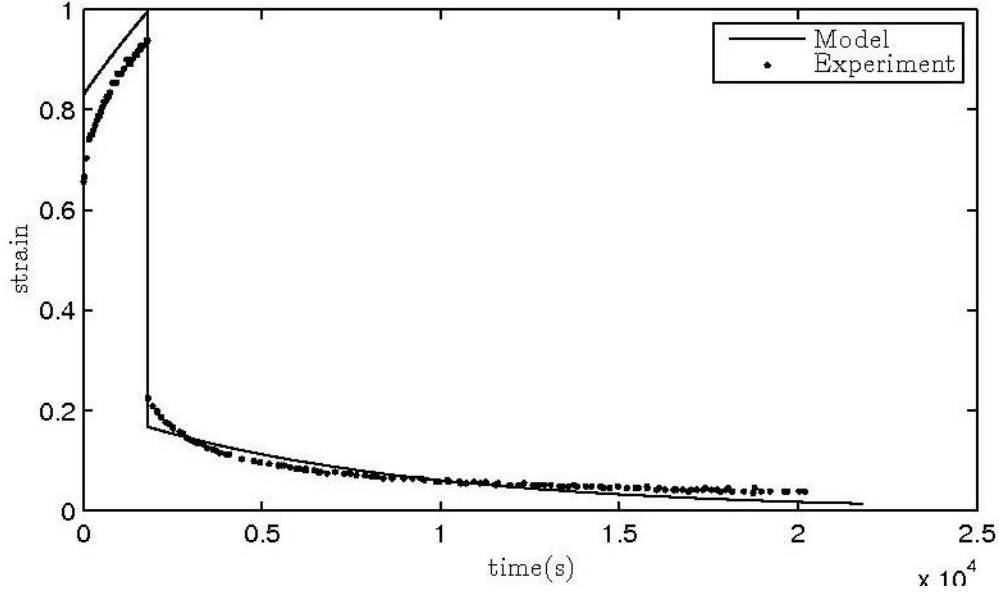
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Figure 1. **Comparison of the model with experimental data for creep (Falcone and Ruggles‑Wrenn (2009)) of PMR‑15 at 288$^{\circ}C$.**

The parameter values used were $\bar{\mu}_G = 4 \times 10^8 \, Pa$, $\bar{\mu}_p = 4 \times 10^8 \, Pa$, $\eta = 6.436 \times 10^{12} \, Pa$, $m = 1$.

The creep data from our model was compared to the experimental creep data of Falcone and Ruggles‑Wrenn (2009) for PMR‑15 at $288°C$. 'fminsearch' function (which uses Nedler‑Mead simplex method) was used to minimize the error defined by

$$error = w \times \sqrt{\frac{\sum \left(\varepsilon_{theo,load} - \varepsilon_{exp,load}\right)^2}{\sum \left(\varepsilon_{exp,load}\right)^2}} + (1-w) \times \sqrt{\frac{\sum \left(\varepsilon_{theo,unload} - \varepsilon_{exp,unload}\right)^2}{\sum \left(\varepsilon_{exp,unload}\right)^2}}, \quad (63)$$

where ε_{theo} denotes the theoretical strain values, ε_{exp} denotes the experimental strain values, the suffixes $load$, $unload$ denote the values during loading and unloading processes respectively, w is weight. A weight of $w = 0.75$ was used since there are fewer data points for the unloading process. The best‑fit values of the parameters were found to be $\bar{\mu}_G = \bar{\mu}_p = 4 \times 10^8 \, Pa$, $\eta = 6.436 \times 10^{12} \, Pa$.

3.0 DIFFUSION OF A NEWTONIAN FLUID THROUGH A VISCOELASTIC SOLID

In this section, we shall extend the model developed in the previous section to include diffusion of a Newtonian fluid (like moisture).

3.1 Preliminaries

Let us consider a mixture of a Newtonian fluid and a viscoelastic solid. We shall also assume co-occupancy of the constituents i.e., at each point $\mathbf{x}$ in the mixture at some time t, the two constituents exist together in a homogenized fashion and are capable of moving relative to each other. We shall denote the quantities associated with the compressible fluid through the superscript f and with the superscript s for that of the solid. Now, we shall define the motion χ^i for the i - th constituent of the mixture through

$$\mathbf{x} = \chi^i \left(\mathbf{X}^i, t \right), \quad i = f, s \tag{64}$$

where $\mathbf{X}^i$ is the material point of the i - th constituent in its reference configuration. We shall assume that the mapping χ^i is sufficiently smooth and invertible at each time t. The velocity associated with the i - th constituent is defined as

$$\mathbf{v}^i = \frac{\partial \chi^i}{\partial t}, \tag{65}$$

and the deformation gradient through

$$\mathbf{F}^i = \frac{\partial \chi^i}{\partial \mathbf{x}^i}. \tag{66}$$

The density ρ and the average velocity (also known as **barycentric** velocity) $\mathbf{v}$ of the mixture are defined by

$$\rho = \sum_i \rho^i, \quad \mathbf{v} = \frac{1}{\rho} \sum_i \rho^i \mathbf{v}^i. \tag{67}$$

We define the following derivatives for any scalar quantity ϕ^i by

$$\frac{\partial \phi^i}{\partial t} = \frac{\partial \tilde{\phi}^i}{\partial t}, \quad \frac{d^i \phi^i}{dt} = \frac{\partial \hat{\phi}^i}{\partial t}, \quad \nabla \phi^i = \frac{\partial \tilde{\phi}^i}{\partial \mathbf{x}}, \quad \frac{\partial \phi^i}{\partial \mathbf{X}^i} = \frac{\partial \hat{\phi}^i}{\partial \mathbf{X}^i}, \tag{68}$$

where

$$\phi^i = \tilde{\phi}^i \left(\mathbf{x}^i, t \right) = \hat{\phi}^i \left(\mathbf{X}^i, t \right). \tag{69}$$

Hence,

$$\frac{d^i \phi^i}{dt} = \frac{\partial \phi^i}{\partial t} + \nabla \phi^i . \mathbf{v}^i, \tag{70}$$

and we shall also define the following

$$\frac{d\phi}{dt} = \frac{\partial \phi}{\partial t} + \nabla \phi . \mathbf{v}. \tag{71}$$

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The velocity gradient for the i - th component $\mathbf{L}^i$ and the velocity gradient for the total mixture $\mathbf{L}$ are defined by

$$\mathbf{L}^i = \nabla \mathbf{v}^i, \quad \mathbf{L} = \nabla \mathbf{v}. \tag{72}$$

$$\rho^i \frac{d}{dt}\left(\epsilon^i + \frac{\mathbf{v}^i.\mathbf{v}^i}{2}\right) = \mathrm{div}\left(\mathbf{T}^i.\mathbf{v}^i - \mathbf{q}^i\right) + \rho^i r^i + \rho^i \mathbf{b}^i.\mathbf{v}^i + E^i + \mathbf{m}^i.\mathbf{v}^i, \tag{73}$$

where ϵ^i, $\mathbf{q}^i$, r^i are the specific internal energy, heat flux, radiant heating associated with the i - th component and E^i is the energy supplied to the i - th constituent from the other constituents.

Now, taking the scalar multiplication of Eqn. (78) and $\mathbf{v}^i$ and subtracting the resulting equation from Eqn. (82), we arrive at

$$\rho^i \frac{d\epsilon^i}{dt} = \mathbf{T}^i.\mathbf{L}^i - \mathrm{div}\mathbf{q}^i + \rho^i r^i + E^i, \tag{74}$$

Now, using $\epsilon^i = \psi^i + \theta\eta^i$, where ψ^i, η^i are the Helmholtz potential and specific entropy of the i - th constituent, with θ being the common temperature of the constituents at a point in the mixture, Eqn. (83) along with Eqn. (76) results in

$$\frac{\partial}{\partial t}\left(\rho^i\eta^i\right) + \mathrm{div}\left(\rho^i\eta^i\mathbf{v}^i\right) = \frac{1}{\theta}\mathbf{T}^i.\mathbf{L}^i - \mathrm{div}\left(\frac{\mathbf{q}^i}{\theta}\right) - \frac{1}{\theta^2}\mathbf{q}^i.\nabla\theta + \frac{1}{\theta}\rho^i r^i + \frac{1}{\theta}E^i$$
$$- \frac{\rho^i}{\theta}\left(\frac{d^i\psi^i}{dt} + \eta^i\frac{d^i\theta}{dt}\right). \tag{75}$$

Now, using the fact that $\eta^i = -\frac{\partial\psi^i}{\partial\theta}$, we can establish the following result:

$$\frac{d^i\psi^i}{dt} + \eta^i\frac{d^i\theta}{dt} = \frac{d^i\psi^i}{dt} - \frac{\partial\psi^i}{\partial\theta}\frac{d^i\theta}{dt} = \left(\frac{\partial\psi^i}{\partial t} - \frac{\partial\psi^i}{\partial\theta}\frac{\partial\theta}{\partial t}\right) + \mathbf{v}.\left(\nabla\psi^i - \frac{\partial\psi^i}{\partial\theta}\nabla\theta\right)$$
$$= \left(\frac{d^i\psi^i}{dt}\right)_{\theta=constant} \tag{76}$$

We shall define

$$\mathbf{q} = \sum_i \mathbf{q}^i, \quad r = \frac{1}{\rho}\sum_i \rho^i r^i \tag{77}$$

Using the relation (85) in Eqn. (84) and summing over i, we get

$$\frac{\partial}{\partial t}\left(\sum_i \rho^i\eta^i\right) + \mathrm{div}\left(\sum_i \rho^i\eta^i\mathbf{v}^i\right) = \frac{1}{\theta}\sum_i \mathbf{T}^i.\mathbf{L}^i - \mathrm{div}\left(\frac{\mathbf{q}}{\theta}\right) - \frac{1}{\theta^2}\mathbf{q}.\nabla\theta + \rho\left(\frac{r}{\theta}\right)$$
$$+ \frac{1}{\theta}\sum_i E^i - \frac{1}{\theta}\sum_i \rho^i\left(\frac{d^i\psi^i}{dt}\right)_{\theta=constant}. \tag{78}$$

Equation (87) is the balance of entropy with the rate of entropy production ζ being

$$\zeta = \frac{1}{\theta}\sum_i \mathbf{T}^i.\mathbf{L}^i - \frac{1}{\theta^2}\mathbf{q}.\nabla\theta + \frac{1}{\theta}\sum_i E^i - \frac{1}{\theta}\sum_i \rho^i\left(\frac{d^i\psi^i}{dt}\right)_{\theta=constant}. \tag{79}$$

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We shall assume that the total entropy production can be additively split into entropy production due to thermal effects i.e., conduction (ζ_c), and entropy production due to internal working and mixing (ζ_m). We shall require due to the second law of thermodynamics that each of these quantities be non‑negative. This implies that

$$\zeta_c := -\frac{\mathbf{q}.\nabla\theta}{\theta^2} \geq 0, \tag{80}$$

$$\zeta_m := \frac{1}{\theta}\sum_i \mathbf{T}^i.\mathbf{L}^i + \frac{1}{\theta}\sum_i E^i - \frac{1}{\theta}\sum_i \rho^i \left(\frac{d^i\psi^i}{dt}\right)_{\theta=constant} \geq 0. \tag{81}$$

We shall choose $\mathbf{q} = -k(\rho,\theta)\nabla\theta,\; k \geq 0$, so that (89) automatically satisfies. Also, if we define the rate of dissipation $\xi_m := \theta\zeta_m$, then

$$\sum_i \mathbf{T}^i.\mathbf{L}^i + \sum_i E^i - \sum_i \rho^i \left(\frac{d^i\psi^i}{dt}\right)_{\theta=constant} = \xi \geq 0. \tag{82}$$

Assuming

$$\sum_i E^i + \sum_i \mathbf{m}^i.\mathbf{v}^i = 0, \tag{83}$$

Eqn. (91) can be re‑written as

$$\sum_i \mathbf{T}^i.\mathbf{L}^i - \sum_i \mathbf{m}^i.\mathbf{v}^i - \sum_i \rho^i \left(\frac{d^i\psi^i}{dt}\right)_{\theta=constant} = \xi_m. \tag{84}$$

Now,

$$\sum_i \rho^i \left(\frac{d^i\psi^i}{dt}\right) = \frac{\partial}{\partial t}\left(\sum_i \rho^i\psi^i\right) + \mathrm{div}\left(\sum_i \rho^i\psi^i\mathbf{v}^i\right)$$
$$= \rho\frac{d\psi}{dt} + \mathrm{div}\left(\sum_i \rho^i\psi^i\left(\mathbf{v}^i - \mathbf{v}\right)\right), \tag{85}$$

where $\psi := \frac{1}{\rho}\sum_i \rho^i\psi^i$ is the average Helmoltz potential of the mixture.

Finally, from eqn (94) and Eqn. (93), we arrive at

$$\sum_i \mathbf{T}^i.\mathbf{L}^i - \sum_i \mathbf{m}^i.\mathbf{v}^i - \left[\rho\frac{d\psi}{dt} + \mathrm{div}\left(\sum_i \rho^i\psi^i\left(\mathbf{v}^i - \mathbf{v}\right)\right)\right]_{\theta=constant} = \xi_m. \tag{86}$$

Assuming that all the components have the same Helmholtz potential (95) reduces to

$$\sum_i \mathbf{T}^i.\mathbf{L}^i - \sum_i \mathbf{m}^i.\mathbf{v}^i - \left(\rho\frac{d\psi}{dt}\right)_{\theta=constant} = \xi_m. \tag{87}$$

3.2 Constitutive assumptions

Let κ_t denote the current configuration of the mixture and let κ_R, κ_r denote the reference configurations of the solid and the fluid respectively. Also, let $\kappa_{p(t)}$ denote the natural configuration of the viscoelastic solid (see Figure 2). Now, if $\mathbf{F}^i,\; i = f,s$ is the gradient of the

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reference configuration of the solid
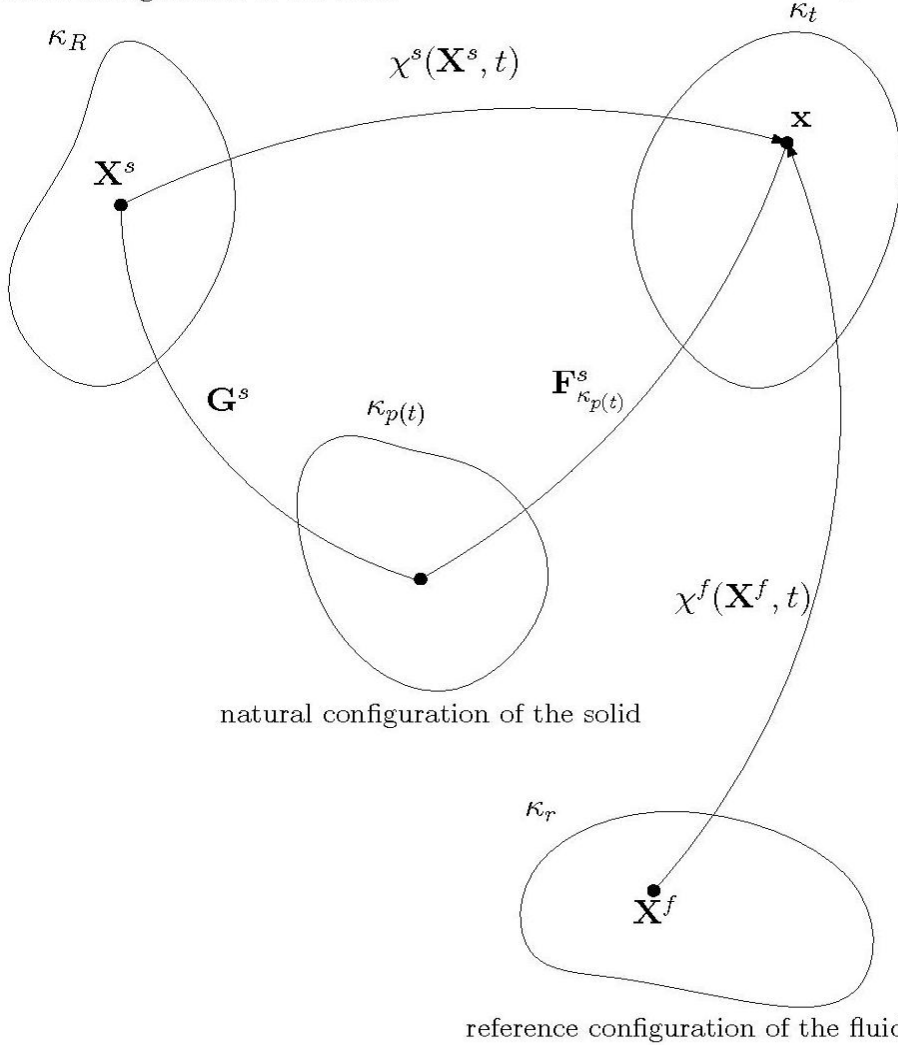
current configuration of the mixture

κ_R

κ_t

$\chi^s(\mathbf{X}^s, t)$

$\mathbf{x}$

$\mathbf{X}^s$

$\mathbf{G}^s$

$\kappa_{p(t)}$

$\mathbf{F}^s_{\kappa_{p(t)}}$

$\chi^f(\mathbf{X}^f, t)$

natural configuration of the solid

κ_r

$\mathbf{X}^f$

reference configuration of the fluid

Figure 2. Constitutive Assumptions

motion (usually known as deformation gradient) $\chi^s\left(\mathbf{X}^\mathbf{i}, t\right)$ and $\mathbf{F}^s_{\kappa_{p(t)}}$ is the gradient of the motion of the viscoelastic solid from $\kappa_{p(t)}$ to κ_t, then

$$\mathbf{G}^s := \mathbf{F}^s \left(\mathbf{F}^s_{\kappa_{p(t)}}\right)^{-1}. \tag{88}$$

We shall assume that the specific Helmholtz potential for the mixture is of the form

$$\psi = \hat{\psi}\left(\theta, I_{B^s_G}, II_{B^s_G}, III_{B^s_G}, I_{B^s_{p(t)}}, II_{B^s_{p(t)}}, III_{B^s_{p(t)}}\right), \tag{89}$$

And

$$\frac{d\psi}{dt} = \frac{d^s\psi}{dt} + (\mathbf{v} - \mathbf{v}^s).\mathrm{grad}\psi \tag{90}$$

$$\Rightarrow \frac{d\psi}{dt} = \left[\left(\frac{\partial\hat{\psi}}{\partial I_{B_{p(t)}}} + I_{B_{p(t)}}\frac{\partial\hat{\psi}}{\partial II_{B_{p(t)}}}\right)\mathbf{I} - \frac{\partial\hat{\psi}}{\partial II_{B_{p(t)}}}\mathbf{B}_{p(t)} - \frac{\partial\hat{\psi}}{\partial III_{B_{p(t)}}}\mathbf{B}^{-1}_{p(t)}\right].\dot{\mathbf{B}}_{p(t)} \tag{91}$$

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$$+ \left[\left(\frac{\partial \hat{\psi}}{\partial I_{B_G}} + I_{B_G} \frac{\partial \hat{\psi}}{\partial II_{B_G}} \right) \mathbf{I} - \frac{\partial \hat{\psi}}{\partial II_{B_G}} \mathbf{B}_G - \frac{\partial \hat{\psi}}{\partial III_{B_G}} \mathbf{B}_G^{-1} \right] . \dot{\mathbf{B}}_G + \frac{\partial \hat{\psi}}{\partial \theta} \dot{\theta} + (\mathbf{v} - \mathbf{v}^s).\mathrm{grad}\psi, \tag{92}$$

where we have dropped the superscript s over $\mathbf{B}_G, \mathbf{B}_{p(t)}$ for convenience, and $\dot{(\ )}$ is $\frac{d^s(\ )}{dt}$.

Now,

$$\dot{\mathbf{F}} = \dot{\mathbf{F}}_{\kappa_{p(t)}} \mathbf{G} + \mathbf{F}_{\kappa_{p(t)}} \dot{\mathbf{G}}$$
$$\Rightarrow \dot{\mathbf{F}} \mathbf{F}^{-1} = \dot{\mathbf{F}}_{\kappa_{p(t)}} \mathbf{G} \mathbf{G}^{-1} \mathbf{F}_{\kappa_{p(t)}}^{-1} + \mathbf{F}_{\kappa_{p(t)}} \dot{\mathbf{G}}$$
$$\Rightarrow \mathbf{L} = \mathbf{L}_{p(t)} + \mathbf{F}_{\kappa_{p(t)}} \mathbf{L}_G \mathbf{F}_{\kappa_{p(t)}}^{-1}$$
$$\Rightarrow \mathbf{D} = \mathbf{D}_{p(t)} + \frac{1}{2} \left(\mathbf{F}_{\kappa_{p(t)}} \mathbf{L}_G \mathbf{F}_{\kappa_{p(t)}}^{-1} + \mathbf{F}_{\kappa_{p(t)}}^{-T} \mathbf{L}_G^T \mathbf{F}_{\kappa_{p(t)}}^T \right), \tag{93}$$

where $\dot{(.)}$ is the time derivative of the second order tensor. In addition,

$$\dot{\mathbf{B}}_{p(t)} = \dot{\mathbf{F}}_{\kappa_{p(t)}} \mathbf{F}^T + \mathbf{F} \dot{\mathbf{F}}_{\kappa_{p(t)}}^T$$
$$= \mathbf{L}_{p(t)} \mathbf{B}_{p(t)} + \mathbf{B}_{p(t)} \mathbf{L}_{p(t)}^T, \tag{94}$$

and similarly

$$\dot{\mathbf{B}}_G = \mathbf{L}_G \mathbf{B}_G + \mathbf{B}_G \mathbf{L}_G^T. \tag{95}$$

Hence, from (102) and (103), we have

$$\dot{\mathbf{B}}_{p(t)} = \mathbf{L} \mathbf{B}_{p(t)} + \mathbf{B}_{p(t)} \mathbf{L}_{p(t)}^T - \mathbf{F}_{\kappa_{p(t)}} \left(\mathbf{L}_G + \mathbf{L}_G^T \right) \mathbf{F}_{\kappa_{p(t)}}^T, \tag{96}$$

Based on the assumption of isotropic elastic response, we choose $\kappa_{p(t)}$ such that

$$\mathbf{F}_{\kappa_{p(t)}} = \mathbf{V}_{\kappa_{p(t)}}, \tag{97}$$

where $\mathbf{V}_{\kappa_{p(t)}}$ is the right stretch tensor in the polar decomposition of $\mathbf{F}_{\kappa_{p(t)}}$.

Using (102), (103), (104), (106) in (101), we get

$$\dot{\psi} = 2 \left[\left(\frac{\partial \hat{\psi}}{\partial I_{B_{p(t)}}} + I_{B_{p(t)}} \frac{\partial \hat{\psi}}{\partial II_{B_{p(t)}}} \right) \mathbf{B}_{p(t)} - \frac{\partial \hat{\psi}}{\partial II_{B_{p(t)}}} \mathbf{B}_{p(t)}^2 - \frac{\partial \hat{\psi}}{\partial III_{B_{p(t)}}} \mathbf{I} \right] . (\mathbf{L}^s - \mathbf{L}_G^s) \tag{98}$$

$$+ 2 \left[\left(\frac{\partial \hat{\psi}}{\partial I_{B_G}} + I_{B_G} \frac{\partial \hat{\psi}}{\partial II_{B_G}} \right) \mathbf{B}_G - \frac{\partial \hat{\psi}}{\partial II_{B_G}} \mathbf{B}_G^2 - \frac{\partial \hat{\psi}}{\partial III_{B_G}} \mathbf{I} \right] . \mathbf{L}_G^s + \frac{\partial \hat{\psi}}{\partial \theta} \dot{\theta} + (\mathbf{v} - \mathbf{v}^s).\mathrm{grad}\psi, \tag{99}$$

Volume additivity constraint:

$$\phi^s + \phi^f = 1, \tag{100}$$

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where $\phi^i = \dfrac{\rho^i}{\rho_R^i}$, $i = s, f$. Also, we shall assume that the constituents are incompressible in their natural states, i.e.,

$$\rho_R^i = \text{constant}. \tag{101}$$

Eqn. (76) using (110) can be re‑written as

$$\frac{\partial \phi^i}{\partial t} + \text{div}\left(\phi^i \mathbf{v}^i\right) = 0, \tag{102}$$

which implies

$$\frac{\partial \sum_i \phi^i}{\partial t} + \text{div}\left(\sum_i \phi^i \mathbf{v}^i\right) = 0 \tag{103}$$

$$\Rightarrow \text{div}\left(\phi^f \mathbf{v}^f + \phi^s \mathbf{v}^s\right) = 0 (\text{using } (109)). \tag{104}$$

Eqn (113) can be re‑written as

$$\phi^s \text{tr}(\mathbf{L}^s) + \phi^f \text{tr}(\mathbf{L}^f) + \mathbf{v}^s.\text{grad}\phi^s + \mathbf{v}^f.\text{grad}\phi^f = 0 \tag{105}$$

Again from (109), we have

$$\text{grad}\phi^s + \text{grad}\phi^f = 0, \tag{106}$$

Hence, using (115) in (114), we arrive at

$$\phi^s \text{tr}(\mathbf{L}^s) + \phi^f \text{tr}(\mathbf{L}^f) + \mathbf{v}_{s,f}.\text{grad}\phi^s = 0, \tag{107}$$

where $\mathbf{v}_{s,f} = \mathbf{v}^s - \mathbf{v}^f$, is the velocity with which the fluid diffuses with respect to the solid.

We shall also assume that the rate of entropy production is of the form

$$\xi_m = \xi_m\left(\mathbf{L}_G^s, \mathbf{F}_{p(t)}^s, \mathbf{L}^f, \theta, \mathbf{v}_{s,f}\right). \tag{108}$$

Now (96) along with (80) reduces to

$$\mathbf{T}^s.\mathbf{L}^s + \mathbf{T}^f.\mathbf{L}^f - \mathbf{m}^s.\mathbf{v}_{s,f} - \left(\rho\frac{d\psi}{dt}\right)_{\theta=constant} = \xi_m\left(\mathbf{L}_G^s, \mathbf{F}_{p(t)}^s, \mathbf{L}^f, \theta, \mathbf{v}_{s,f}\right). \tag{109}$$

Using (108) in (118), we get

$$\mathbf{T}^s.\mathbf{L}^s + \mathbf{T}^f.\mathbf{L}^f - \mathbf{m}^s.\mathbf{v}_{s,f} - \mathbf{T}_{p(t)}^s.\left(\mathbf{L}^s - \mathbf{L}_G^s\right) - \mathbf{T}_G^s.\mathbf{L}_G^s - \rho(\mathbf{v} - \mathbf{v}^s).\left(\text{grad}\psi\right)_{\theta=constant}$$
$$= \xi_m\left(\mathbf{L}_G^s, \mathbf{F}_{p(t)}^s, \mathbf{L}^f, \theta, \mathbf{v}_{s,f}\right), \tag{110}$$

where

$$\mathbf{T}_{p(t)}^s := 2\rho\left[\left(\frac{\partial\hat{\psi}}{\partial I_{B_{p(t)}}} + I_{B_{p(t)}}\frac{\partial\hat{\psi}}{\partial II_{B_{p(t)}}}\right)\mathbf{B}_{p(t)} - \frac{\partial\hat{\psi}}{\partial II_{B_{p(t)}}}\mathbf{B}_{p(t)}^2 - \frac{\partial\hat{\psi}}{\partial III_{B_{p(t)}}}\mathbf{I}\right], \tag{111}$$

$$\mathbf{T}_G^s := 2\rho \left[\left(\frac{\partial \hat{\psi}}{\partial I_{B_G}} + I_{B_G} \frac{\partial \hat{\psi}}{\partial II_{B_G}} \right) \mathbf{B}_G - \frac{\partial \hat{\psi}}{\partial II_{B_G}} \mathbf{B}_G^2 - \frac{\partial \hat{\psi}}{\partial III_{B_G}} \mathbf{I} \right]$$

(112)

Eqn. (119) with the constraint (116) can be written as

$$\mathbf{T}^s.\mathbf{L}^s + \mathbf{T}^f.\mathbf{L}^f - \mathbf{m}^s.\mathbf{v}_{s,f} - \mathbf{T}_{p(t)}^s.(\mathbf{L}^s - \mathbf{L}_G^s) - \mathbf{T}_G^s.\mathbf{L}_G^s - \rho(\mathbf{v} - \mathbf{v}^s).(\mathrm{grad}\psi)_{\theta=constant}$$
$$+ \lambda \left(\phi^s \mathrm{tr}(\mathbf{L}^s) + \phi^f \mathrm{tr}(\mathbf{L}^f) + \mathbf{v}_{s,f}.\mathrm{grad}\phi^s \right) = \xi_m \left(\mathbf{L}_G^s, \mathbf{F}_{p(t)}^s, \mathbf{L}^f, \theta, \mathbf{v}_{s,f} \right)$$

(113)

We shall further assume that the rate of dissipation can be additively split into the rate of dissipation due to mechanical working, rate of dissipation due to the fluid and the rate of dissipation due to diffusion of the fluid, with specific forms as follows:

$$\xi_m \left(\mathbf{L}_G^s, \mathbf{F}_{p(t)}^s, \mathbf{L}^f, \theta, \mathbf{v}_{s,f} \right) = \xi \left(\mathbf{L}_G^s, \mathbf{B}_{p(t)}, \theta \right) + \nu \mathbf{D}^f.\mathbf{D}^f + \alpha(\theta)\mathbf{v}_{s,f}.\mathbf{v}_{s,f}.$$

(114)

Then, from (123) and (122), we arrive at

$$\mathbf{T}^s.\mathbf{L}^s + \mathbf{T}^f.\mathbf{L}^f - \mathbf{m}^s.\mathbf{v}_{s,f} - \mathbf{T}_{p(t)}^s.(\mathbf{L}^s - \mathbf{L}_G^s) - \mathbf{T}_G^s.\mathbf{L}_G^s - \rho(\mathbf{v} - \mathbf{v}^s).(\mathrm{grad}\psi)_{\theta=constant}$$
$$+ \lambda \left(\phi^s \mathrm{tr}(\mathbf{L}^s) + \phi^f \mathrm{tr}(\mathbf{L}^f) + \mathbf{v}_{s,f}.\mathrm{grad}\phi^s \right) = \xi \left(\mathbf{L}_G^s, \mathbf{B}_{p(t)}, \theta \right) + \nu \mathbf{D}^f.\mathbf{D}^f + \alpha(\theta)\mathbf{v}_{s,f}.\mathbf{v}_{s,f}$$

(115)

which can be re- written as

$$\mathbf{L}^s.\left[\mathbf{T}^s + \lambda\phi^s\mathbf{I} - \mathbf{T}_{p(t)}^s \right] + \mathbf{L}^f.\left[\mathbf{T}^f + \lambda\phi^f\mathbf{I} - \nu\mathbf{D}^f \right] + \left(\mathbf{T}_{p(t)}^s - \mathbf{T}_G^s \right).\mathbf{L}_G^s$$
$$+ \mathbf{v}_{s,f}.\left[-\mathbf{m}^s + \lambda \,\mathrm{grad}\phi^s - \alpha(\theta)\mathbf{v}_{s,f} + \rho^f \,(\mathrm{grad}\psi)_{\theta=constant} \right] = \xi \left(\mathbf{L}_G^s, \mathbf{B}_{p(t)}, \theta \right),$$

(116)

using the fact that $\rho \left(\mathbf{v} - \mathbf{v}^s \right) = \rho^f \mathbf{v}_{s,f}$. Since, the right hand side of (125) does not depend on $\mathbf{L}^s$, $\mathbf{L}^f$ and $\mathbf{v}_{s,f}$, we have

$$\mathbf{T}^s = -\lambda\phi^s\mathbf{I} + \mathbf{T}_{p(t)}^s,$$

(117)

$$\mathbf{T}^f = -\lambda\phi^f\mathbf{I} + \nu\mathbf{D}^f,$$

(118)

$$\mathbf{m}^s = \lambda \,\mathrm{grad}\phi^s - \alpha(\theta)\mathbf{v}_{s,f} + \rho^f \,(\mathrm{grad}\psi)_{\theta=constant},$$

(119)

and so (125) reduces to

$$\left(\mathbf{T}_{p(t)}^s - \mathbf{T}_G^s \right).\mathbf{L}_G^s = \xi \left(\mathbf{L}_G^s, \mathbf{B}_{p(t)}, \theta \right)$$

(120)

Now, we have

$$\rho_R^s = \rho^s J^s = \rho^s J_G^s J_p^s,$$

(121)

where $J_k^s = det(\mathbf{F}_k^s)$, $k = G, p$ or no subscript. From (110) and (130) and further assumption that there is no diffusion of mass from $\kappa_{p(t)}$ to κ_t, we have

$$J_G^s = constant \Rightarrow \frac{d^s J_G^s}{dt} = 0 \Rightarrow \mathrm{tr}\mathbf{L}_G^s = 0.$$

(122)

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Next, we shall maximize the rate of dissipation ξ with (129) and (130) as constraints. We shall maximize the auxillary function

$$\Phi := \xi + \beta\left[\xi - \left(\mathbf{T}^s_{p(t)} - \mathbf{T}^s_G\right).\mathbf{L}^s_G\right] + \mu\left(\mathbf{I}.\mathbf{L}^s_G\right) \tag{123}$$

Now,

$$\frac{\partial \Phi}{\partial \mathbf{L}^s_G} = 0 \Rightarrow \frac{(\beta+1)}{\beta}\frac{\partial \xi}{\partial \mathbf{L}^s_G} - \left(\mathbf{T}^s_{p(t)} - \mathbf{T}^s_G\right) + \frac{\mu}{\beta}\mathbf{I} = 0. \tag{124}$$

Taking the scalar product of (133) with $\mathbf{L}^s_G$ and using (129), (131)

$$\frac{(\beta+1)}{\beta} = \frac{\xi}{\frac{\partial \xi}{\partial \mathbf{L}^s_G}.\mathbf{L}^s_G}. \tag{125}$$

Next, taking the trace of (133)

$$\frac{\mu}{\beta} = \frac{1}{3}\left[\text{tr}\left(\mathbf{T}^s_{p(t)} - \mathbf{T}^s_G\right) - \frac{\xi}{\frac{\partial \xi}{\partial \mathbf{L}^s_G}.\mathbf{L}^s_G}\text{tr}\left(\frac{\partial \xi}{\partial \mathbf{L}^s_G}\right)\right]. \tag{126}$$

The evolution equation for the natural configuration of the solid is given by

$$\left(\mathbf{T}^s_{p(t)} - \mathbf{T}^s_G\right) = \frac{\mu}{\beta}\mathbf{I} + \frac{\xi}{\frac{\partial \xi}{\partial \mathbf{L}^s_G}.\mathbf{L}^s_G}\frac{\partial \xi}{\partial \mathbf{L}^s_G} \tag{127}$$

We shall assume the following specific form for the specific Helmholtz potential of the mixture

$$\hat{\psi} = A^s + (B^s + c^s_2)(\theta - \theta_s) - \frac{c^s_1}{2}(\theta - \theta_s)^2 - c^s_2\theta\ln\left(\frac{\theta}{\theta_s}\right) + \frac{\mu_{G0} - \mu_{G1}\theta}{2\rho\theta_s}(I_{B_G} - 3) + \frac{\mu_{p0} - \mu_{p1}\theta}{2\rho\theta_s}(I_{B_{p(t)}} - 3), \tag{128}$$

where $\mu_{G0}, \mu_{G1}, \mu_{p0}, \mu p1$ are elastic constants, θ_s is a reference temperature for the viscoelastic solid

Now,

$$s = -\hat{\psi}\theta$$
$$= -(B^s + c^s_2) + c^s_1(\theta - \theta_s) + c^s_2\ln\left(\frac{\theta}{\theta_s}\right) + c^s_2 + \frac{\mu_{G1}}{2\rho\theta_s}(I_{B_G} - 3) + \frac{\mu_{p1}}{2\rho\theta_s}(I_{B_{p(t)}} - 3). \tag{129}$$

The internal energy ϵ is given by

$$\epsilon = \psi + \theta s$$
$$= A^s - B^s\theta_s + c^s_2(\theta - \theta_s) + \frac{c^s_1}{2}(\theta^2 - \theta^2_s) + \frac{\mu_{G0}}{2\rho\theta_s}(I_{B_G} - 3) + \frac{\mu_{p0}}{2\rho\theta_s}(I_{B_{p(t)}} - 3). \tag{130}$$

and the specific heat capacity C_v is

$$C_v = -\epsilon\theta = c^s_1\theta + c^s_2. \tag{131}$$

From (137) and (120)

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$$\mathbf{T}^s_{p(t)} = \frac{\rho}{\rho^s_R} \frac{J^s_p J^s_G \theta}{\theta_s} \left[\mu_p \mathbf{B}_{p(t)} - \frac{\mu_p}{2(J^s_p)^2} \left(I_{B_{p(t)}} - 3 \right) \mathbf{I} - \frac{\mu_G}{2(J^s_p)^2} \left(I_{B_G} - 3 \right) \mathbf{I} \right],$$

$$\tag{132}$$

and from (137) and (121),

$$\mathbf{T}^s_G = \frac{\rho}{\rho^s_R} \frac{J^s_p J^s_G \theta}{\theta_s} \left[\mu_G \mathbf{B}_G - \frac{\mu_p}{2(J^s_G)^2} \left(I_{B_{p(t)}} - 3 \right) \mathbf{I} - \frac{\mu_G}{2(J^s_G)^2} \left(I_{B_G} - 3 \right) \mathbf{I} \right],$$

$$\tag{133}$$

where $\mu_G = \mu_{G0} - \mu_{G1}\theta$, $\mu_p = \mu_{p0} - \mu_{p1}\theta$.

We shall further assume that the rate of dissipation ξ is of the form

$$\xi = \gamma(\theta) \mathbf{D}_G . \mathbf{D}_G, \tag{134}$$

then (126) becomes

$$\mathbf{T}^s = -\lambda \phi^s \mathbf{I} + \frac{\rho\theta}{\rho^s \theta_s} \left[\mu_p \mathbf{B}_{p(t)} - \frac{\mu_p}{2(J^s_p)^2} \left(I_{B_{p(t)}} - 3 \right) \mathbf{I} - \frac{\mu_G}{2(J^s_p)^2} \left(I_{B_G} - 3 \right) \mathbf{I} \right]$$

$$\tag{135}$$

and (136) reduces to

$$\frac{\rho\theta}{\rho^s \theta^s} \left\{ \mu_p \mathbf{B}_{p(t)} - \mu_G \mathbf{B}_G - \frac{1}{3} \left[\mu_p \mathrm{tr}(\mathbf{B}_{p(t)}) - \mu_G \mathrm{tr}(\mathbf{B}_G) \right] \mathbf{I} \right\} = \gamma(\theta) \mathbf{D}_G$$

$$\tag{136}$$

The final constitutive equations are

$$\mathbf{T}^s = -\lambda \phi^s \mathbf{I} + \frac{\rho}{\rho^s} \left[\bar{\mu}_p \mathbf{B}_{p(t)} - \frac{\bar{\mu}_p}{J^s_p} \left(I_{B_{p(t)}} - 3 \right) \mathbf{I} - \frac{\bar{\mu}_G}{J^s_p} \left(I_{B_G} - 3 \right) \mathbf{I} \right]$$

$$\mathbf{T}^f = -\lambda \phi^f \mathbf{I} + \nu \mathbf{D}^f,$$

$$\mathbf{m}^s = \lambda \, \mathrm{grad}\phi^s - \alpha(\theta)\mathbf{v}_{s,f} + \rho^f \left(\mathrm{grad}\psi \right)_{\theta=constant},$$

$$\tag{137}$$

where $\bar{\mu}_p = \dfrac{\mu_{p0} - \theta\mu_{p1}}{\theta^s}$, $\bar{\mu}_G = \dfrac{\mu_{G0} - \theta\mu_{G1}}{\theta^s}$ with

$$\frac{\rho}{\rho^s} \left\{ \bar{\mu}_p \mathbf{B}_{p(t)} - \bar{\mu}_G \mathbf{B}_G - \frac{1}{3} \left[\bar{\mu}_p \mathrm{tr}(\mathbf{B}_{p(t)}) - \bar{\mu}_G \mathrm{tr}(\mathbf{B}_G) \right] \mathbf{I} \right\} = \gamma(\theta) \mathbf{D}_G$$

$$\tag{138}$$

being the evolution equation of the natural configuration.

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